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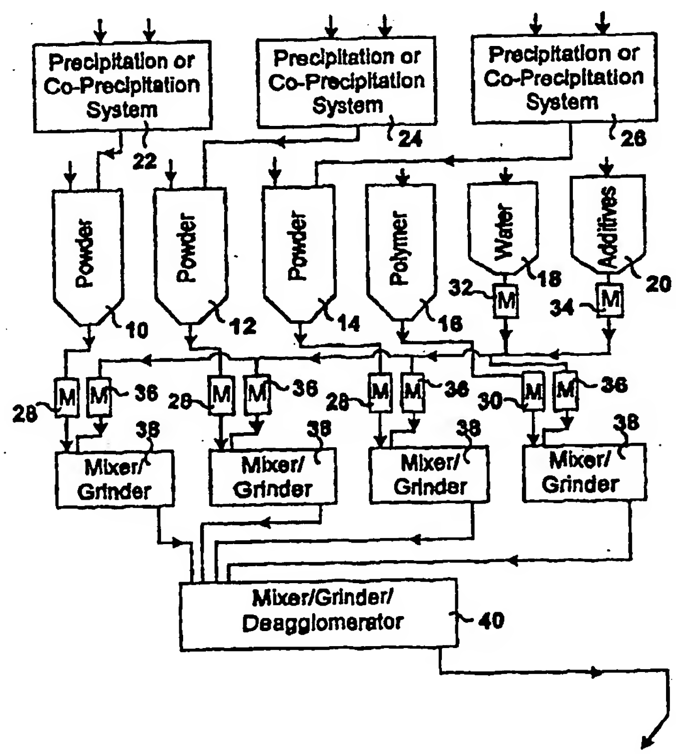
(57) Abstract

Composite materials comprising at least 70 volume % of particles of finely powdered inorganic material in a matrix of polymer material are made by forming separate mixtures of the components in respective liquid dispersion media, mixing the mixtures to produce thorough dispersion of the components together, dewatering the mixture and forming green articles therefrom. The green articles are heated and pressed to a temperature sufficient to melt the polymer and to a pressure sufficient to disperse the melted polymer into the interstices between the inorganic particles. Mixtures of different inorganic materials may be used to tailor the electrical and physical properties of the final materials. The inorganic materials may be obtained in finely divided form by precipitation or coprecipitation. The articles preferably comprise substrates for use in electronic circuits. The invention also comprises apparatus for carrying out the method and the composite materials that result.. Polymer particles of required small size are made by cooling a strip or rod to a brittle fracture temperature and feeding it against a moving grinding surface of coarseness to produce the particles.



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MANUFACTURE OF COMPOSITES OF INORGANIC POWDER AND POLYMER MATERIALS

CROSS-REFERENCE TO A RELATED APPLICATION

Insofar as this application constitutes an application in the U.S.A. it is a continuation-in-part of my earlier application Serial No. 08/738,612, filed 29 October 1996 (29.10.96), pending, for which the benefit of 35USC120 is also claimed.

TECHNICAL FIELD

The invention is concerned with methods and apparatus for the manufacture of composite materials consisting of particles of finely powdered inorganic material bonded in a matrix of polymer material, and new composite materials made with such methods and apparatus. The invention is also concerned more specifically, but not exclusively, with such methods, apparatus, and new composite materials, in which high melting point thermoplastic polymers are employed as matrix forming materials. The invention is also concerned with new methods and apparatus for producing particles of finely powdered polymer for use as matrix forming materials in such composite materials.

BACKGROUND ART

The electronics industry is an example of one which makes substantial use of substrates as supports for the electronic circuits, such substrates consisting of thin flat pieces produced to exacting specifications as to starting material and physical, dielectric, thermal and loss characteristics. In the earliest history of the electronics industry such a substrate was usually referred to as the "chassis", and the only physical characteristics considered to be important were its strength and light weight, so that the material of choice commonly was thin

sheet steel or aluminium. Subsequently "circuit boards" were developed in which the signal carrying insulated copper wires previously used were replaced by metal strips bonded to a substrate consisting of an insulating material, eventually usually some form of glass fibre reinforced thin sheet polymer material coated with a thin layer of copper, which was then back-etched to produce the electric circuit.

The history of the industry also shows the use of progressively higher operating frequencies and currently, for example, for frequencies up to about 800 megahertz (MHz), copper coated circuit boards of glass fibre reinforced epoxies, cyanide esters, PTFE and polyimides are used, the most popular having the quality designation "FR-4". At higher frequencies these materials also are no longer suitable, primarily because of unacceptable losses and also anisotropic thermal expansion problems with fluctuating operating temperatures of the substrate, owing to the relatively large coefficients of thermal expansion of the polymers usable as substrate material, and the unequal expansion coefficients of glass fibers in their length and thickness dimensions. For frequencies above 800MHz and far into the gigahertz (GHz) spectrum the materials of choice are certain ceramics of appropriate dielectric constant, formed by sintering or firing suitable powdered inorganic materials, such as fused silica; alumina; aluminum nitride; barium titanate; barium titanate complexes such as $Ba(Mg_{1/3}Ti_{2/3})0_2$, $Ba(Zr,Sn)TiO_4$, and $BaTiO_3$ doped with Sc_2O_3 and rare earth oxides, alkoxy-derived $SrZrO_3$ and $SrTiO_3$; and pyrochlore structured Ba(Zr,Nb) oxides. Substrates have also been employed consisting of metal powders and semiconductor powders embedded in a glass or polymer matrix.

For example, such ceramic substrates used for hybrid electronic circuit applications often comprise square plates of 5cm (2ins) side, their production usually involving the step of preparing a "slip" (slurry) of the finely powdered material dispersed in a suitable liquid

dispersion vehicle, dewatering the slip to a stiff leathery mixture, making a "green" preform from the mixture, and then sintering the preform to become the final substrate plate with the desired properties. The substrates are required to have highly uniform values of thickness, grain size, grain structure, density, surface flatness and surface finish, with the purpose of obtaining uniform dielectric, thermal and chemical properties, and also to permit the application to the surfaces of fine lines of conductive or resistive metals or inks, usually in the range 10 micrometers to 0.6mm (0.00004in to 0.024in) in width and of thicknesses ranging from 0.76g/sqcm to 0.61g/sqcm (0.125oz/ft^2 to 2oz/ft^2), these being values obtained with copper conductors. The goal is to minimize losses, maximize signal speeds and to facilitate matching of the impedances of the circuit components. As a specific example, thick film substrates manufactured from alumina have an alumina content of 96.0%-99.9%, a range of grain sizes from 0.1-50 micrometers, and a bulk density of 3.75-3.9, the latter figure being almost the maximum available. They must have a minimum surface finish of less than 0.75-0.90 micrometer (30-40 microinches) for thick film usage, and about 0.05 micrometer (2 microins) for thin film usage, with an absence of abrasive damage, a camber tolerance of 0.003mm/mm (0.003 in/in), and a thickness tolerance of ±0.38mm (±0.0015 in); in many applications much finer tolerances than these may be required. One reason for such stringent requirements is, for example, that pores in the material, such as those between sintered ceramic can absorb conductive material printed thereon, resulting in considerable deviations from the theoretical design values in performance. Also, the passage of such circuit lines over too rough a surface, caused by the presence of large grains, results in an increase in conductor length and unpredictable corresponding increases in resistance. This problem is exacerbated by the drive in the industry to use even thinner circuit lines, and lines as thin as 0.6 micrometer are sometimes used.

Such sintered products inherently contain a number of special and very characteristic types of flaws. A first consists of fine holes created by the entrainment of bubbles in the slip and causing residual porosity in the body; these bubble holes may have sizes in the range about 1-20 micrometers and the bubbles that form them cannot be removed from the slip by known methods. As an example, sintered alumina substrates are frequently found to have as many as 800 residual bubble holes per sq/cm of surface (5,000 per sq/in). Another flaw is triple-point holes at the junctions of the rounded ceramic granules when the substrate has been formed by roll-compacting; they may also result from uneven powder flow during the compaction, and they are of similar size to the bubble holes and appear in similar numbers per sq/cm. Yet another consists of "knit-lines", which are webs or networks of seam lines of lower density formed at the contact areas between butting particles during cold pressing. Two other characteristic flaws are caused by inclusions of foreign matter into the material during processing, and the enlarged grains caused by agglomeration of the particles, despite their initial fine grinding. The usual inclusions are fine metal particles due to abrasive wear of the mixers, owing principally to the inherently hard and abrasive nature of the starting materials employed. Agglomeration is caused by weak interparticle forces that are particularly effective on small particles, to the extent that dry powders with an average particle size less that 10 micrometers will agglomerate spontaneously. Once an agglomerate has formed the particles may then become bound together by stronger chemical bonding forces, so that they can only be separated by regrinding. Both inclusions and agglomerates will sinter in a matrix at a different rate from the majority of the matrix and stresses that result can result in flaws of much greater magnitude than the original inclusion or agglomerate. For example alumina powder of 1 micrometer average particle size will readily agglomerate to particles in the range 20-50 micrometers, in turn resulting

in sintered grains of about 100 micrometers, rendering the substrate commercially useless.

Ceramic articles with such critical properties and tolerances can only be obtained when the starting material is of very small particle size, i.e. average particle size of one micrometer or less, and by the use of sintering aids and schedules that minimise the growth of grains from these particles. Any such flaws present in the green ware are amplified during the heating, and cracks and fractures in the finished products are almost always initiated at the regions containing them. In addition to their tendency to initiate cracks, the flaws also have deleterious effects on properties such as thermal shock resistance, dielectric strength, loss tangent and high temperature deformation, and for ceramic products intended for high strength applications flaws as small as 10 micrometers may still be too large. Because of the difficulty with existing manufacturing methods of avoiding small dimension flaws, ceramic parts for high strength applications may require proof testing of every part, considerably increasing their cost. Because of shape changes caused by shrinkage during the sintering process, and the intrinsic difficulty of obtaining the required smooth and uniform surfaces, the substrates often require costly surface finishing by diamond grinding and polishing making the processes and products more expensive. The statistical reliability, or relative absence of catastrophic failure, of ceramic products commonly is characterised by the so-called "Weibull" number, a low (poor) value of which is about 2, an average value is in the range 5-10, a good value is 15, and an exceptional value is in the range 20-25. The diamond grinding and polishing typically produce micro-cracks and micro-scratches that reduce the Weibull number to the low and average values with a consequent relatively high rejection rate.

A limitation is found in the use of sintered ceramic materials for electronic substrates when attempts

are made to form a ceramic from co-sintered mixtures of the materials, in order to try to blend and thus tailor their different physical and electrical properties for specific applications. It is often impossible to incorporate even small amounts of a different material or materials, e.g. up to about 10-15% by weight, into a body of ceramic material by such co-sintering without serious disruption of the structure during the sintering because of difference in morphology changes of the respective grains, as well as problems with mutual wetting during the period that the temperature rises into the sintering range; such disruption can be so severe that the body becomes a heap with the appearance of loose sand.

Ferroelectric sintered ceramic materials with very desirable high dielectric constants of between 2,000 and 3,000 are available, for example barium titanate, but difficulty is experienced in using them for high frequency applications, such as wireless telecommunication devices, owing to sever non-linearity in their dielectric constant/temperature characteristic over the usual operating temperature range of 0°C to 200°C. Thus, a considerable, non-linear, peak-like increase in dielectric constant (referred to as the Curie peak) occurs at the so-called Curie temperature (frequently between 120°C and 160°C) and renders the materials non-usable because of corresponding peak-like changes in circuit parameters. At the present time the highest temperature-stable dielectric constant that can be achieved with sintered ceramics is between 90 and 100. However, H.C. Graham, N.M. Tallan and K.S. Mazdiazni in their paper "Electrical Properties of High-Purity Polycrystalline Barium Titanate", Journal of The American Ceramic Society, Vol. 54, No. 11, described the interesting discovery that the Curie peak almost disappears when the barium titanate is heated to not more than about 700°C, instead of the value 1350°C necessary for full densification sintering. Materials with temperature stable dielectric constants of 500 and above would be especially valuable when

making gigahertz frequency resonators, since their size, weight and cost could be reduced by more than a factor of two.

There is therefore increasing interest in methods and apparatus for manufacturing methods composite materials for electronic substrates, such as are used for resonators, frequency filters, and electronic packaging materials, with which sintering and the high processing temperatures required, together with their difficulties as described above and the associated considerable cost, are completely avoided.

DISCLOSURE OF INVENTION

The principal object of the invention is to provide new methods and apparatus for manufacturing composite materials consisting of particles of finely powdered inorganic material bonded together in a matrix of polymer material, such new composite materials, and articles made from such composite materials.

It is another object to provide such new methods and apparatus with which the composite materials and articles can comprise at least 70 percent by volume of the finely powdered inorganic material, with the remainder consisting of the polymer material matrix.

It is a further object to provide such new methods and apparatus, composite materials and articles, in which thermoplastic, high temperature stable polymers, such as polyimides and liquid crystal polymers, are employed as matrix forming materials.

It is a further object to provide new methods and apparatus for producing particles of finely powdered polymer for use in such methods and apparatus.

In accordance with the invention there is provided a method of manufacturing composite materials comprising particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles together, the method comprising the steps of:

mixing together particles of finely powdered inorganic material and a liquid dispersion medium to form a flowable mixture thereof;

mixing together particles of finely powdered polymer material and a liquid dispersion medium to form a flowable mixture thereof;

mixing together the two flowable mixtures to form a flowable composite mixture thereof;

removing liquid dispersion medium from the flowable composite mixture and forming green articles from the resulting composite mixture; and

subjecting the green articles to a temperature sufficient to melt the polymer material and to a pressure sufficient to disperse the melted polymer material into the interstices between the particles of inorganic material.

Also in accordance with the invention there is provided apparatus for manufacturing composite materials comprising particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles together, the apparatus comprising:

means for mixing together particles of finely powdered inorganic material and a liquid dispersion medium to form a flowable mixture thereof;

means for mixing together particles of finely powdered polymer material and a liquid dispersion medium to form a flowable mixture thereof;

means for mixing together the two flowable mixtures to form a flowable composite mixture thereof;

means for removing liquid dispersion medium from the flowable composite mixture and for forming green articles from the resulting composite mixture;

heated pressing means in which the green articles are placed, the pressing means being adapted to subject the green articles to a temperature sufficient to melt the polymer material and to a pressure sufficient disperse the melted polymer material into the interstices between the particles of inorganic material.

Further in accordance with the invention there are provided composite materials comprising particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles:

wherein the quantity of the polymer material is that required to fill the interstices between the closely packed particles of inorganic material;

wherein the material has been produced by subjecting a mixture of particles of the inorganic material together with particles of the polymer material to a temperature sufficient to melt the polymer material and to a pressure sufficient to disperse the melted polymer material into the interstices between the particles of inorganic material.

Further in accordance with the invention there is provided a method of producing particles of a polymer material in finely powdered form, the method comprising:

cooling a strip or rod of the polymer material to a temperature at which the material is subject to brittle fracture; and

feeding the cooled strip or rod into contact with a moving grinding surface of coarseness required to produce polymer particles of less than the desired maximum size.

Further in accordance with the invention there is provided apparatus for producing particles of a polymer material in finely powdered form, the apparatus comprising:

means for cooling a strip or rod of the polymer material to a temperature at which the material is subject to brittle fracture;

a moving grinding surface of coarseness required to produce polymer particles at and less than the desired maximum size; and

means for feeding the cooled strip or rod into contact with the moving grinding surface.

DESCRIPTION OF THE DRAWINGS

Methods and apparatus, and materials and articles produced using such methods and apparatus, that are particular preferred embodiments of the invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings wherein:

Figures 1A and 1B together in sequence constitute a block flow diagram of a specific method and apparatus for the manufacture of composite materials and articles of the invention, particularly for the manufacture of flat rectangular copper coated substrates intended for use for electronic circuits;

Figure 2 is a part cross section to a greatly enlarged scale through a small piece of a typical material of the invention in order to show the grain structure thereof;

Figure 3 is a longitudinal cross section through apparatus for the manufacture of particles of finely powdered polymer materials;

Figure 4 is an enlarged view of part of the apparatus of Figure 3 taken on the line 4-4 therein; and

Figure 5 is a more enlarged view in plan of part of the apparatus of Figures 3 and 4.

MODES FOR CARRYING OUT THE INVENTION

Referring now to Figure 1, a first step in any of the methods of the invention is to form a preliminary mixture of each of the selected finely powdered inorganic materials, and each of the selected finely powdered polymers, with a suitable liquid dispersion vehicle,

preferably water because of its ready availability and ease of subsequent disposal. A very effective way of obtaining the required inorganic material or mixture of materials of suitable particle size directly is respectively by precipitation or coprecipitation from solutions of suitable precursors. However obtained, the finely powdered inorganic material should have the required purity, dielectric constant, loss tangent, and particle size distribution. In this embodiment from one to up to three different powdered materials can be fed from a delivery and metering system comprising a series of hoppers 10, 12 and 14 respectively, while a single powdered polymer material, or polymer material mixture, is fed from its hopper 16, water is fed from its hopper 18, and suitable surface active functional additives, such as surfactants, plasticizers and lubricants, are fed from their hopper 20. In other embodiments one or two or more than three powder hoppers may be employed, and more than one polymer, liquid medium and additive hoppers may be employed. In this embodiment each powdered material or mixture can be fed directly to the respective hopper 10, 12, or 14, or alternatively any one or more can be obtained from respective precipitation or coprecipitation systems 22, 24, or 26. The flow of each inorganic powder from its hopper is continuously precision metered by a respective meter 28, that of the polymer powder is metered by meter 30, those of the water and surface active additives are metered by respective meters 32 and 34, and those of the combined water/additive flows are metered by respective meters 36. Each preliminary mixture of powder, polymer, water and additives is delivered into a respective drum type mixer/grinding mill 38, described in more detail below. Prior to the formation of each mixture the respective powder particles usually consist of random and widely varying agglomerations of many finer particles and this must be corrected. Each mixer/mill 38 operates as a mixing/dispersing means to produce complete dispersion of the powdered material in the dispersion vehicle, and also as a grinding mill to mill the respective powder particles, and

the agglomerates that are present, to a required size and to a size distribution that will facilitate the subsequent stages of the process.

The proportions of the powder, water and additives from the hoppers are such as to obtain a solids content in the respective preliminary mixture in the range of 40-70% by volume, the quantities of the dispersing vehicle and the functional additives being kept as low as possible but sufficient for the consistency of the mixture to be kept to that of a relatively wet paste or slurry, to permit its free flow through the relatively narrow flow processing passages of the respective mill 38, and the subsequent processing machines. A viscosity in the range of about 100-10,000 centipoises will usually be satisfactory. In the methods and apparatus of the invention preferably such grinding, deagglomeration and dispersion of each preliminary mixture is carried out simultaneously in its respective mill 38, using for this purpose a special mill which is the subject of my U.S. Patents Nos. 5,279,463, issued 18 January, 1994, and 5,538,191 issued 23 July, 1996, the disclosures of which are incorporated herein by this reference.

These special mills may be of two major types, in a first of which the mill has two circular coaxial plate members with a processing gap formed between them; the axis of rotation can be vertical or horizontal. It is preferred however to use in these processes the second type of mill, which consists of an inner cylinder member rotatable about a horizontal axis inside a stationary hollow outer cylinder member, the axes of the two cylinders being slightly displaced so that the facing walls are more closely spaced together at the bottom point around their periphery to form what is referred to as a processing or micro gap, and are more widely spaced at the top point to form what is referred to as a complementary or macro gap. The mixture flows through the processing gap while the mill members move relative to one another transversely to the direction of

flow, the relative motions producing so-called "super-Kolmorgoroff" mixing eddies in the portion of the slurry at and close to the macro gap and so-called "sub-Kolmorgoroff" mixing eddies in the micro or processing gap. Ultrasonic transducers may be mounted on the stationary member which apply longitudinal pressure oscillations into the gap; these oscillations reverberate between the two closely spaced surfaces and produce and reinforce the "sub-Kolmorgoroff" mixing eddies. Such apparatus is capable of processing relatively thick slurries of sub-micrometer particles in minutes that otherwise can take several days in conventional high shear mixers and ball or sand mills.

The separate preliminary mixtures are now mixed together, in proportion of powders and polymer that will be discussed below, to form a combined mixture having the consistency of a uniform wet paste, while at the same time they are subjected to another grinding, deagglomerating and uniform dispersing operation by passing them into a mill 40, which again is one of the above-mentioned special mills which are the subject of my Patents Nos. 5,279,463 and 5,538,191. The mill 40 is also of the type comprising an inner cylinder member rotatable inside a stationary hollow outer cylinder member. Although only a single mill 40 is employed in this embodiment, in some processes it may be preferred to employ a chain of two or more such mills depending upon the amount and rate of grinding, deagglomeration and mixing that is required. The mills 38 and 40 may be self-pumping, so that additional pumps are not required to move the wet paste through the apparatus, although such separate additional pumps can be used if appropriate for the particular process. Each produces its own positive effect so that the initial single mixtures and the subsequent multiple mixture achieve an increasingly constant particle size distribution as it moves down the chain, this constancy in particle size distribution also increasing with the number of mills in the chain until a distribution of the required uniformity has been obtained.

The processing of any particular single mixture will usually involve a particular protocol which inter-relates the process time and the height of the processing gap of the mill, in dependence upon the physical nature and the state of the powder as received from the manufacturer. Thus the process is initiated in the respective first mill 38, in which the processing gap may be relatively large in case any large agglomerates are present, and the processing gap spacing in the subsequent mill 40 or mills 40 in series will be at the final desired value. It will usually be most effective to operate an individual mill with a relatively limited particle size range, and for example a mill with a feed in the range 0-100 micrometers will be employed to produce a product in the range 0-10 micrometer (0-10,000 nanometers) while one with a feed in the range 0-10 micrometers will be employed to produce a product in the range 0-0.2 micrometer (0-200 nanometers). Similarly, a mill with a feed in the range 0-0.2 micrometer (0-200 nanometers) will be employed to produce a product in the range 0-0.08 micrometer, (0-80 nanometers).

The wet paste produced by the mill 40, or by the last mill in the series, is fed to a tape casting machine of any known type, represented schematically herein by the doctor blade 42 forming the casting gate, in which the paste is cast as an endless tape of uniform width and thickness. The tape is deposited on an endless conveyor 44, which passes it through a drying oven 46 during which all of the water and as much as possible of the additives are removed to leave the tape consisting only of a thoroughly and uniformly dispersed mixture of the particles of the inorganic material or materials and particles of the polymer or polymers. A suitable temperature for such an oven is, for example, in the range 80-120°C, the drying being carried out slowly to avoid as far as possible the formation of bubble holes by the exiting dispersion medium. If the time and temperature obtained in the oven 46 is not sufficient to remove all of the additives, the substrates

may be passed through a microwave drying oven 48, in which they are heated internally, for more efficient drying. It is important however to ensure that the polymer material is not exposed to temperatures too close to its melting temperature. It is preferred to remove as much liquid as possible, but a lower limit is set by the need to be able conveniently to handle and process the stiff pasty material that results. The conveyor ends in a station 50 in which the tape of dried paste is severed into individual "green" substrate preforms 52, usually of rectangular shape and of the size required for the electronic circuit board substrate, if that is the use for which the materials are intended.

The preforms are then deposited manually or automatically into the cavity of a heated compression mold comprising heated upper and lower platens 54 and 56 respectively. The cavity is located in the lower heated platen 56 to facilitate the loading process. Once the preform is loaded the mold cavity is closed by the downward moving heated top platen 56 which protrudes into the cavity to compress the preform to its required dimensions and density. The temperature to which the preforms are heated in the mold is sufficient to melt the polymer, while the pressure and time for which the mold is closed is sufficient for the material of the preforms to attain maximum density. During the heat and pressure cycle the melted polymer will flow relatively freely and the temperature and pressure are maintained for a period sufficient to ensure that the polymer can flow to completely fill the interstices between the solid particles. Typically this pressure is in the range 70MPa to 1,380 MPa (10,150 to 200,000 psi). The surfaces of the platens that contact the preforms are mirror-finished or better to assist in obtaining the smooth surfaces that are desired for electronic substrates intended for microwave frequency applications.

The raw substrates issuing from the press are fed to a multi-stand flattening roller mill 58 of known type in which they are rolled to an accurately controlled thickness and flattened. The surfaces of these rolls are also mirror-finished or better, again in order to obtain the desired smooth surfaces. Substrates intended for use in electronic circuits will usually be of thickness in the range 0.125mm to 1.5mm (0.005in to 0.060in), and if intended for thick film usage are usually required to be flat to about 0.75-0.90 micrometer (22-40 microins), while if intended for thin film usage must be flat to about 0.05 micrometer (2 microins). It is an important advantage of the methods and apparatus of the present invention that the substrates can be produced with such surface finishes by relatively inexpensive low temperature molding and rolling steps, instead of the more expensive grinding and polishing required for ceramic substrates. They are now fed to a heated laminating press 60 in which they are each laminated on one or both sides with a thin flat smooth piece 62 of copper sheet of the same size, which subsequently is etched in known manner to produce the electric circuit. The substrate preforms 52 will always have a certain amount of the polymer at their surfaces, and the adhesive property of the polymer is sufficient to bond the copper sheet firmly onto the surface without the need for other adhesive, although an adhesive can be applied if appropriate. These sheet copper pieces are obtained by cutting from a strip 64 supplied from a roll thereof (not shown) which is cut into pieces at a cutting and mirror-finish surfacing station 66. The surfacing means comprises a hot press in which the cut pieces are pressed between a pair of heated platens, the platen surfaces being mirror-finished or better so that a corresponding finish is imparted to the surfaces of the pieces. For example, the copper pieces will be of thickness in the range 0.0038g/sqcm to 0.0610g/sqcm (0.125oz/sq.ft to 2.0oz/sq.ft), will be subjected to a temperature in the range 200oC to 50% of the respective

melting temperature of the copper, and to a pressure in the range 70MPa to 350MPa (10,000psi to 50,000psi).

The methods and apparatus of the invention are particularly applicable to the production of composite materials in which the finely powdered inorganic material consists of any one or a mixture of the "advanced" materials that are now used in industry for the production of fired ceramic substrates for electronic circuits, the most common of which are aluminum nitride; barium titanate; barium-neodymium titanate; barium copper tungstate; lead titanate; lead magnesium niobate; lead zinc niobate; lead iron niobate; lead iron tungstate; strontium titanate; zirconium tungstate; the chemical and/or physical equivalents of any of the foregoing; alumina; fused quartz; metal powders; and semiconductors. Owing to the economy possible in the production of electronic substrates, resonators and filters by the methods and apparatus of the invention, it is possible to use these materials in the production of metal coated circuit boards, as well as in uncoated substrates, taking advantage of their superior electrical and physical properties over those of glass fibre reinforced polymer materials or over those of sintered and machined ceramic materials currently in use.

Another important group of materials to which the invention is particularly applicable is compositions including as the inorganic component materials of higher elrctric induction capability, if the composition is already inductive, or capable of introducing induction if none is present in their absence. Compositions comprising powdered ferrites and like inductive materials in a polymer matrix have already been produced, used for example in magnetic passive products such as transformers, inductors and ferrite core devices, but the methods used add the powdered inorganic material into the polymer matrix by mixing as described above, and accordingly their solids contents have generally been limited to not more than about 50% by volume

for the reasons already explained. The invention permits the production of such composite materials of higher solids content, e.g. 70% by volume and above. The use of the invention also avoids the difficulties involved in prior art techniques of producing inductive elements when the materials are sintered. As described above, the use of high dielectric constant materials is advantageous in attempting to miniaturize substrates at high frequencies. High dielectric constant is particularly helpful with miniaturization of capacitive circuit elements, since the capacitance increases with the dielectric constant, but impedance matching of all circuit elements is important and the inductance may also need to be increased in order to maintain the overall impedance constant. The addition of inductors at strategic locations is possible, but adds to the cost. An alternative provided by the invention is to add inductance introducing or enhancing powders, such as powdered ferrite, to the high dielectric powder in proportion determined by suitable experimentation and then processing the resultant mixture in accordance with the invention to form the substrates. A product to which this aspect of the invention is particularly applicable is the so-called "patch" antenna used in mobile telecommunications equipment, consisting of a square or rectangular element applied in the form of a patch; these can be made smaller and more easily mounted, facilitating the desired miniaturization of the equipment. The methods of the invention avoid the problems and failures encountered if it is attempted to sinter incompatible mixtures of highly inductive materials, such as ferrites, which are usually also at least weakly magnetic, with ceramic high dielectric constant materials. Other problems encountered in prior art processes with these inductive materials are the severe segregation that takes place during conventional wet batch type powder mixing due to density differences, and the inherent strong agglomeration that takes place with suspended particles due to their magnetic properties. These problems are avoided since the materials are processed

as stiff pastes rather than slurries, so that the particles have no freedom to flocculate and/or agglomerate and/or settle preferentially.

The composite materials of the invention have a number of advantages over the glass fibre, polymer fibre, and PTFE reinforced materials used hitherto. For example all polymers have relatively large coefficients of expansion, for example of the order of 60 X 10^{-6}mm/mm/°C, whereas values of the order of 5-6 X 10^{-6}mm/mm/°C are desired. Although they are added mainly for their expansion restraining capabilities, reinforcing whiskers and fibres, woven or unwoven, are characterised by considerable differences in thermal expansion coefficients along their crossectional axes, as compared to their longitudinal axes, the crossectional coefficient frequently being many times that of the longitudinal coefficient; which can lead to rupture of the metal conductors plated through holes in the substrate to connect the circuits on both sides. In addition, the thermal expansion mismatches that exist between the metal conductors, the integrated circuits bonded to the surfaces, and the polymer material can lead to metal and chip separations or breakage. Furthermore, such polymers and their reinforcements have dielectric constants of the order of 0.26 to 10, which are only really satisfactory with operating frequencies below about 800MHz.

At this time the only ceramic materials with temperature stable dielectric constants that are available have values in the range 20 to 90, whereas in the quickly expanding market of wireless telecommunication, which is based on microwave frequencies ranging from 800MHz to over 30GHz, and in which small size and low weight are of increasing importance, the preferred dielectric constant values are of the order of between 400 and 2000. The reason for requiring such high dielectric constants is the fact that in microwave or GHz frequencies signal propagation depends mainly on the waveguide character of the circuitry

and consequently only such high dielectric constant materials allow significant miniaturization, permitting the use of much narrower conductor line widths and shorter lengths. For example, coaxial dielectric resonators, at this time used in more than 25 million cellular telephones worldwide, could be reduced in size weight by more than half and in cost by more than two thirds, if the dielectric constant of the substrate material could be raised from the present value of 90 to over 400 and its dielectric loss (loss tangent) kept below 0.0005. The problems described above when attempting to sinter ceramics have hitherto prevented the successful manufacture and application of such materials.

An unexpected very important advantage of the invention is the ability to fabricate composite materials in which the powdered inorganic material is a blend of two or more individual materials, which as described above cannot be formed by sintering into a strong coherent body. The requirements for substrate materials, especially for very high frequency applications, are very exacting, requiring consideration of a large number of physical properties including alumina content, bulk density (range), surface finish, grain size (average), water absorption(%), flexural strength, modulus of elasticity, coefficient of linear thermal expansion, thermal conductivity, dielectric strength, dielectric constant, dissipation factor, and volume resistivity. The possibility of such blending, when necessary or desirable, is facilitated by the process step of individual dispersion of each material and subsequent mixing to a combined dispersion, making it possible to tailor the properties of the substrates to their specific tasks in a manner which is not possible with a sintered ceramic. One of the main reasons for combining inorganic materials in any given ratio is to obtain a mixture with as high a dielectric constant as possible which will remain constant over a temperature range from say -50°C to +200°C, and a very high Q factor (equivalent to a very low loss

tangent, 1/Q) desirable above 500 and if possible as high as 5,000.

For example, alumina is commonly used because of its overall excellent high strength characteristics, high abrasion resistance and relatively low cost, despite the disadvantages of its mediocre heat conductivity and relatively low dielectric constant. Boron nitride is sometimes preferred because of its superior heat conductivity, but has the disadvantage of a low dielectric constant of only 4.2. Fused silica is sometimes preferred because of its very low dielectric loss tangent, but has the disadvantage that its thermal conductivity is very low. Titanium tungstate is sometimes preferred because of its negative coefficient of thermal expansion, but used by itself as an electronic substrate will cause too great a thermal expansion mismatch with most other materials. Barium nanotitanate is sometimes preferred because of its somewhat higher dielectric constant, but has disadvantages of being very brittle in the sintered state and having low heat conductivity. By its elimination of sintering the present invention enables the use in electronic substrates of, for example, temperature stable barium titanate materials with dielectric constants in the range 2,000 to 3,000. If, in a specific example, a barium titanate of a dielectric constant of 2,000 is mixed with 30 volume% of a polyimide polymer, which is the maximum amount of polymer contemplated for the materials of the invention, then according to Looyenga's mixing rule (H. Looyenga, "Dielectric Constants of Heterogeneous Mixtures", Physica 31, [3] 401-406, 1965) the dielectric constant of the resultant mixture is 799, which is still substantially higher than the value of 90 to 100, as mentioned above, obtainable with the sintered material, and well above the "dream" value of 500 at present sought by the manufacturers of these products.

The present invention permits any two or more chemically different materials to be mixed in any proportion to achieve a composite material of optimum value for the most important physical or electrical characteristics, the inorganic powder components being bound with a relatively small volume percent of a suitable high strength polymer binder.

It is known to produce a mixture of a powdered inorganic material and a polymer where the inorganic material acts as a filler and polymer binds the particles together. Such composite materials are produced by methods and in heavy compounding machines, such as double screw machines, which require that the inorganic powders be "loaded" into the melted polymer, it being found in practice that it is impossible to obtain a uniform mixture by introducing the polymer material into the inorganic material. Such "loading" has strict limits on how many volume percent of inorganic powder can be introduced into the polymer before the viscosity prevents the mixture from being processable. The problem is exacerbated as the particle size decreases and the effective surface area to be coated with the polymer increases. In such processes when the particle size is in the range 5-30 micrometers it is found in practice impossible to increase the content of the inorganic material above about 55%-60% by volume, and even at these relatively low solids contents the viscosities are so high that powerful machines must be used. As the solids content is increased the mixture becomes so solid that the screws can no longer work, or alternatively the pressures required to keep them moving become impossibly high. Solids contents of 55%-60% by volume can be obtained as long as the average particle size of the inorganic material is above 1 micrometer, but decrease rapidly as the average particle size falls below this value to about 20%-30% by volume, which is so low as to not be worth the effort of making a substrate from the resultant mixture.

With the processes and apparatus of the invention the volume percentage of the inorganic material can be increased to 70% or more, the maximum value being set by the amount of the particular polymer required to adequately bind the particular inorganic material to form a strong coherent body. Thus, they enable the production of composite materials in which the solids content is easily and economically in the range 70%-97% by volume, as will be discussed below, depending upon the particle size distribution, shape and porosity of the inorganic component. The volume fraction of the polymer in the mixtures is only that needed to fill the pores left in the inorganic powder after compression in the mold to high density. The relatively small amounts of polymer present in the composite materials of the invention must be extremely well and evenly dispersed among the fine particles, and this is readily achievable with the processes and apparatus employed virtually independently of the particle size of the inorganic material.

Thus the processes and apparatus of the invention permit the rapid and economical production of the necessary thoroughly dispersed intimate mixture of very high proportions of finely divided inorganic material and relatively smaller proportions of finely divided polymer material without encountering the barriers found with the sintering and compounding processes and apparatus used hitherto, and the subsequent rapid and economical processing of these mixtures to produce the final substrates. Figure 2 is a photo micrograph cross section through a material of the invention, consisting of closely packed particles 68 of the inorganic material, of irregular size and shape, coated and bound together by polymer material 70 that no longer exists as discrete particles but as thin intervening films and interstice-filling masses. As an indication of the size of the particles, etc. involved the square section of Figure 2 measures 5 micrometers each side. Although the various powders of inorganic material could be mixed

together and fed to the appropriate hopper 10, 12, or 14 as a single component, preferably advantage is taken of the economical and superior dispersion provided by the methods and apparatus of the invention to mix them together while simultaneously mixing them with the polymer.

The process variables to be considered during the formulation of the combined mixture and in the hot pressing step in the heated press 54,56 are the relative proportions of the inorganic materials and of the polymer, the particle sizes preferred for use in the composite materials, and the temperature and the pressure employed in the press.

The relative proportions of the inorganic materials and of the polymer depend at least to some extent upon the use to which the substrate is to be put; if a very high frequency circuit is to be installed then it will be preferred to have the maximum amount of inorganic dielectric material and the minimum amount of polymer. The minimum amount of polymer is set by that required to fill the intergrain interstices when the interstitial volume is at its minimum value, and to ensure sufficient coating of the grains for the resulting composite to have the required mechanical strength; for this reason the composites of the invention require a minimum of 3% by volume of polymer to be present as long as the optimum particle packing of the inorganic material has been obtained, the remaining 97% solids content comprising the inorganic dielectric material, residual surface active and coupling agents, and organic or inorganic reinforcing, strength-providing fibres and whiskers.

Materials of relatively small particle sizes are preferred both for the polymers and the inorganic starting materials used in the processes of this invention, and the preferred particle size range for the polymers is from 0.1 to 50 micrometers, while the preferred particle size range for the inorganic starting materials is from 0.01 to 50

micrometers. With ceramics the particle size distribution is an important criterion for flaw reduction, and particularly the requirement that all of the particles are of a size within a narrow range about the nominal value. In industrial practice the achievement of such uniformity of particle size has been extremely difficult and considerably increases the cost of production. It is an unexpected advantage of the invention that there is no longer a requirement for the narrowest possible range of particle sizes for the inorganic materials, and instead the presence of particles of different sizes is preferred, since this improves the capability of dense packing in a manner that reduces the interstitial volume, and consequently reduces the amount of polymer required to fill the interstices and adhere the particles together. It can be shown theoretically that the minimum interstitial volume that can be obtained when packing spheres of uniform size is about 26%. With the materials of the invention, owing to the wider particle size distribution that can be employed, this volume can be reduced considerably further, down to the specified value of about 3%.

The temperatures to be employed in the press are set by the polymer that is chosen as the matrix material. Thus the minimum is that required for the polymer to flow freely under the pressure applied in order to fill the interstices and coat the inorganic material particles, while the maximum is that at which the polymer will begin to degrade.

The minimum pressure to be employed in the press is coupled with the choice of temperature, in that it must be sufficient for the melted polymer to flow as described. The pressure is also dependent to some extent on the particle size and particle size distribution. The denser packing of small, wide size distribution particles, and the very large increase in surface area which they represent, means that higher pressures will be required to achieve

uniform dispersion of the polymer matrix than with larger more uniform size particles. The minimum pressure required for operation of the methods of the invention will be about 3.5MPa (500psi). In addition to causing the required flow of the polymer, the pressure applied to the preforms presses the solid particles of the powdered inorganic materials into more intimate contact with one another, minimizing the interstitial volume. It is believed at present that an extreme upper limit for the pressures employed will be about 1,380MPa (200,000psi) while an upper limit that is at present more commercially likely is 345MPa (50,000psi).

With such small amounts of polymer employed as matrix material to fill the interstices and to adhere the inorganic material particles together, then clearly the choice of polymer material requires careful consideration. many suitable polymers are available such as expoxies, fluoropolymers, cyanide esters, and liquid crystal polymers. An especially suitable family of currently available polymers, many of whose members are particularly suitable for this purpose, is the polyimides. These comprise a very large group of materials which are of considerable commercial interest, and can be thermosetting or thermoplastic. The interest for use in the present invention results from their outstanding properties as structural materials as, for example, high temperature resistance up to 300oC, strength, toughness, hardness and shape retention, solvent and creep resistance, low dielectric constant, low dielectric loss factor, low flammability and low water absorption. These new materials are highly adhesive in nature and self bonding and therefore are especially suited for use as the matrix forming material, which can then be processed at temperatures below the glass transition temperature. Important properties making some of them especially suitable as matrix cements for composite materials for electronic applications is that they are thermoplastic and that their water absorption is very low.

Polymers are not generally available commercially in powder form, and particularly are not available commercially in the small particle size required for the satisfactory performance of the invention. Polyimide polymers are available in flake form, which is not readily reducible to powder form, and Figures 3-5 illustrate a method and apparatus by which a satisfactory finely divided polymer product can be produced. Thus the polymer is purchased in strip or rod form, in either of which it is readily obtainable, the apparatus shown being designed to use strip that has been slit from polymer sheet, but which can readily be adapted to use the rod form. A strip 72 is fed from a reel 74 thereof, rotatably mounted on a standard 76, which is in turn mounted on an apparatus base 78. The strip is led by a guide roller 80 to pass over the upward-open mouth of a bath 82 containing a suitable cooling medium 84, the strip closing the mouth of the bath to inhibit loss of the coolant to the ambient atmosphere, and to ensure intimate contact of the strip with the coolant. The coolant is at a temperature such that during passage of the strip over the bath it will cool the polymer material to a temperature below that at which it is brittle and will fracture easily; examples of suitable coolants are solid carbon dioxide in alcohol acting as a transfer medium and liquid nitrogen. The nature of the coolant should be such that it will evaporate readily after the strip has left the bath without leaving any residue on the strip.

The strip is pulled from the roll 74 and through the bath 82 by a pair of motor-driven feed rolls 86 between which the strip passes. The feed rolls press the end of the brittle strip strongly and progressively against a moving grinding surface which in this embodiment is provided by the cylindrical surface of a rotatably mounted motor driven grinding wheel 88. The grinding surface 90 of the wheel is of the coarseness required to produce particles at and less than the desired maximum value, the particles discharging downwards under the effect of the rotation of the wheel via

a funnel 92 to a hopper 94. The friction of the strip against the grinding surface will of course generate heat, and to ensure that the temperature of the polymer does not rise above that at which brittle fracture will occur, a nozzle or series of nozzles 96 may be provided that directs a stream of coolant along the line of contact of the strip with the grinding surface. In this embodiment the moving grinding surface is serrated in a plane perpendicular to its direction of movement to increase the effective area of surface contact between the strip 72 and the grinding surface 90. The surface is cylindrical and the serrations are therefore disposed in a plane radial to the axis of rotation of the grinding wheel, the serrations being of triangular shape in plan with the apices of the triangles protruding radially outward. Such a method and apparatus is capable of producing economically polymer particles within the range of size and size distribution such that they can be supplied directly to the respective hopper 16 and fed therefrom as the resultant suspension.

The processes of the invention have been described in connection with the manufacture of thin flat plates, but it will be apparent that they are applicable also to any shape of molded article with which direct production of superior surface finish, highly uniform micro-structures, and high dimensional uniformity from finished article to article is desired.

INDEX OF REFERENCE SIGNS

10. Powdered material hopper
12. Powdered material hopper
14. Powdered material hopper
16. Polymer material hopper
18. Water hopper
20. Hopper for surfactants, plasticizers and lubricants
22. Precipitation or coprecipitation system
24. Precipitation or coprecipitation system
26. Precipitation or coprecipitation system
28. Inorganic powder meter
30. Polymer powder meter
32. Water meter
34. Surface active additives meter
36. Combined water/additive flow meters
38. Drum type mixer/grinding mill
40. Drum type mixer/grinding mill
42. Casting gate doctor blade
44. Conveyor
46. Drying oven
48. Microwave drying oven
50. Severing station
52 Green substrate preforms
54. Mold heated upper platen
56. Mold heated lower platen
58. Multi-stand flattening roller mill
60. Heated laminating press
62. Piece of copper sheet
64. Copper strip
66. Mirror-finish surfacing station
68. Closely packed particles of inorganic material
70. Interposed polymer material
72. Polymer strip for grinding
74. Polymer strip reel
76. Strip reel standard
78. Apparatus base

80. Guide roller
82. Bath for cooling medium
84. Cooling medium
86. Motor-driven feed rolls for strip 72
88. Motor driven grinding wheel
90. Grinding wheel grinding surface
92. Funnel for ground material
94. Hopper for ground material

I CLAIM:

1. A method of manufacturing composite materials comprising particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles together characterised by the steps of:

mixing together particles of finely powdered inorganic material and a liquid dispersion medium to form a flowable mixture thereof;

mixing together particles of finely powdered polymer material and a liquid dispersion medium to form a flowable mixture thereof;

mixing together the two flowable mixtures to form a flowable composite mixture thereof;

removing liquid dispersion medium from the flowable composite mixture and forming green articles from the resulting composite mixture; and

subjecting the green articles to a temperature sufficient to melt the polymer material and to a pressure sufficient to disperse the melted polymer material into the interstices between the particles of inorganic material.

2. A method as claimed in claim 1, characterised in that the particles of inorganic material are of size in the range 0.01 to 50 micrometers.

3. A method as claimed in claim 1 or 2, characterised in that the particles of polymer material are of size in the range 0.1 to 50 micrometers.

4. A method as claimed in any one of claims 1 to 3, characterised in that the polymer comprises from 3% to 30% by volume of the composite material and the inorganic material and residual materials comprise the remainder.

5. A method as claimed in any one of claims 1 to 4, characterised in that the green articles are subjected to a pressure in the range 3.5MPa to 1,380MPa (500psi to

200,000psi), preferably in the range 70MPa to 1,380MPa (10,150psi to 200,00psi).

6. A method as claimed in any one of claims 1 to 5, characterised in that the particles of inorganic material consist of a mixture of inorganic materials of different chemical compositions.

7. A method as claimed in any one of claims 1 to 6, characterised in that each inorganic material and the polymer material is mixed individually with a liquid dispersion medium to form a respective flowable mixture and subsequently the flowable mixtures are combined to form a combined mixture.

8. A method as claimed in any one of claims 1 to 7, characterised in that a single inorganic material is produced in finely divided state by precipitation thereof, and a mixture of inorganic materials is produced in finely divided state by coprecipitation thereof.

9. A method as claimed in any one of claims 1 to 8, characterised in that the plastic and inorganic materials are each mixed with a liquid dispersion medium in a respective drum type grinding apparatus as disclosed in U.S. Patents Nos. 5,279,463 and 5,538,191, and in that the flowable combined mixture is mixed in at least one drum type grinding apparatus as disclosed in U.S. Patents Nos. 5,279,463 and 5,538,191.

10. A method as claimed in any one of claims 1 to 9, characterised in that the combined mixture is formed into a tape from which the green articles are cut, and in that the heated and pressed articles are subjected to a rolling operation to flatten them and to render their thickness uniform.

11. A method as claimed in any one of claims 1 to 10, characterised in that the heated and pressed articles are coated on at least one side with a thin layer of copper, and in that the thin layer of copper is subjected prior to such coating to a hot pressing operation between mirror-surfaced platens to render its surfaces correspondingly smooth.

12. A method as claimed in any one of claims 1 to 11, characterised in that the particles of polymer material are of polyimide polymer, in that the particles of inorganic material are selected from the group of materials consisting of alumina, barium titanate, zirconia, silicon nitride, aluminum nitride and lead magnesium niobate, and in that the dispersing medium is water plus functional surface active additives.

13. A method as claimed in any one of claims 1 to 12, characterised in that the particles of polymer material are produced by a method comprising:

cooling a strip or rod of the polymer material to a temperature at which the material is subject to brittle fracture; and

feeding the cooled strip or rod into contact with a moving grinding surface of coarseness required to produce particles of and less than the desired maximum size.

14. Apparatus for manufacturing composite materials comprising particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles together characterised by:

means for mixing together particles of finely powdered inorganic material and a liquid dispersion medium to form a flowable mixture thereof;

means for mixing together particles of finely powdered polymer material and a liquid dispersion medium to form a flowable mixture thereof;

means for mixing together the two flowable mixtures to form a flowable combined mixture thereof;

means for removing liquid dispersion medium from the flowable composite mixture and for forming green articles from the resulting composite mixture; and

heated pressing means in which the green articles are placed, the pressing means being adapted to subject the green articles to a temperature sufficient to melt the polymer material and to a pressure sufficient to disperse the melted polymer material into the interstices between the particles of inorganic material.

15. Apparatus as claimed in claim 14, characterised in that it is for use with inorganic material consisting of a mixture of inorganic materials of different chemical compositions, the apparatus being characterised by:

means for mixing individually each inorganic material and the polymer material with a liquid dispersion medium to form a respective flowable mixture and means for subsequently combining the flowable mixtures to form a combined mixture.

16. Apparatus as claimed in claim 14 or 15, characterised in that means for mixing each of the polymer material and the inorganic material with a liquid dispersion medium is a respective drum type grinding apparatus as disclosed in U.S. Patents Nos. 5,279,463 and 5,538,191, and in that means for mixing the composite mixture is one or a series of drum type grinding apparatus as disclosed in U.S. Patents Nos. 5,279,463 and 5,538,191.

17. Composite materials characterised in that they comprise particles of finely powdered inorganic material in a matrix of polymer material bonding the inorganic material particles together, such materials also being characterised in that:

the particles of the inorganic material are bound together with the quantity of the polymer material required to fill the interstices between the particles of inorganic material;

and in that the material has been produced by subjecting a mixture of particles of the inorganic material together with particles of the polymer material to a temperature sufficient to melt the polymer material and to a pressure sufficient to disperse the melted polymer material into the interstices between the particles of inorganic material.

18. Composite materials as claimed in claim 17, characterised in that the particles of inorganic material consist of a mixture of inorganic materials of different chemical constitutions.

19. Composite materials as claimed in claim 17 or 18, characterised in that the particles of inorganic material are of size in the range 0.01 to 50 micrometers.

20. Composite materials as claimed in any one of claims 17 to 19, characterised in that the polymer comprises from 3% to 30% by volume of the composite material and the inorganic and residual materials comprise the remainder.

21. Composite materials as claimed in any one of claims 17 to 20, characterisedin that they are for use as substrates for electronic circuits.

22. A method of producing particles of a polymer material in finely powdered form characterised by:

cooling a strip or rod of the polymer material to a temperature at which the material is subject to brittle fracture;

feeding the cooled strip or rod into contact with a moving grinding surface of coarseness required to produce particles of and less than the desired maximum size.

23. A method as claimed in claim 22, characterised in that the strip or rod is cooled by passing it over the

surface of a bath containing a cooling medium and in contact with the cooling medium.

24. A method as claimed in claim 22 or 23, characterised in that the strip or rod closes the corresponding surface of the bath containing the cooling medium.

25. A method as claimed in any one of claims 22 to 24, characterised in that the moving grinding surface is serrated in a plane perpendicular to its direction of movement to increase the effective area of surface contact between the strip and the surface.

26. A method as claimed in any one of claims 22 to 25, characterised in that cooling medium is fed to the area of contact of the strip or rod with the moving grinding surface to maintain the strip at a temperature at which the polymer material is subject to brittle fracture.

27. Apparatus for producing particles of a polymer material in finely powdered form characterised by:

means for cooling a strip of the polymer material to a temperature at which the material is subject to brittle fracture;

a moving grinding surface of coarseness required to produce particles at and less than the desired maximum value; and

means for feeding the cooled strip into contact with the moving grinding surface.

28. Apparatus as claimed in claim 27, characterised in that the apparatus comprises means for cooling the strip or rod by passing it over the surface of a bath containing a cooling medium and in contact with the cooling medium.

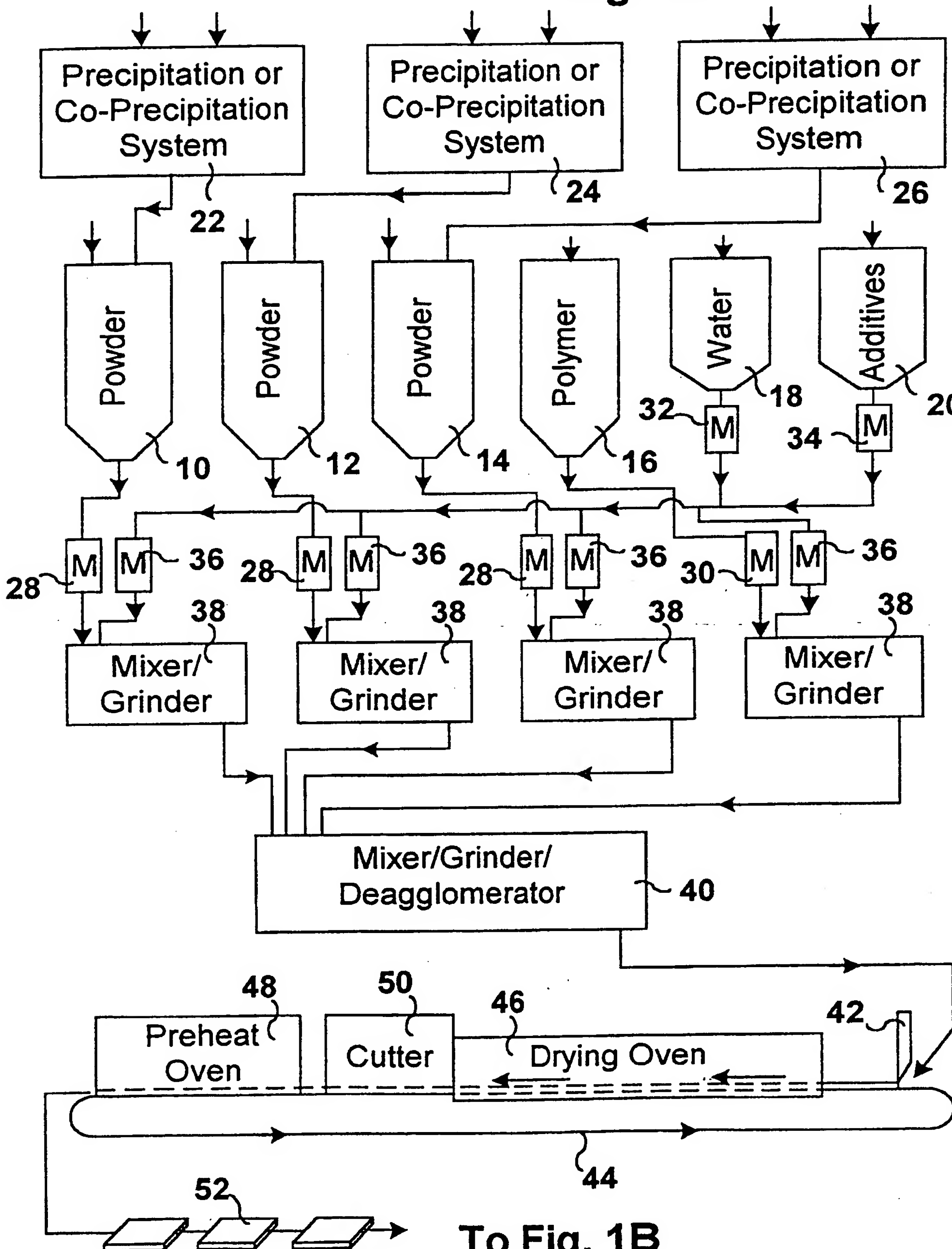
29. Apparatus as claimed in claim 27 or 28, characterised in that the strip or rod closes the

corresponding surface of the bath containing the cooling medium.

30. Apparatus as claimed in any one of claims 27 to 29, characterised in that the moving grinding surface is serrated in a plane perpendicular to its direction of movement to increase the effective area of surface contact between the strip and the surface.

31. Apparatus as claimed in any one of claims 27 to 30, characterised in that the apparatus comprises means for feeding cooling medium to the area of contact of the strip or rod with the moving grinding surface to maintain the strip at a temperature at which the polymer material is subject to brittle fracture.

Fig. 1A



To Fig. 1B

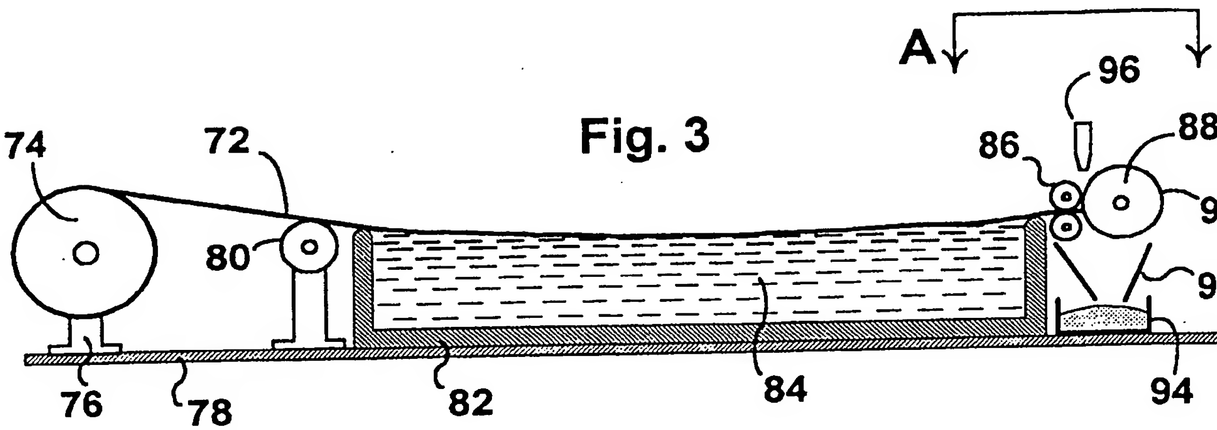


Fig. 3

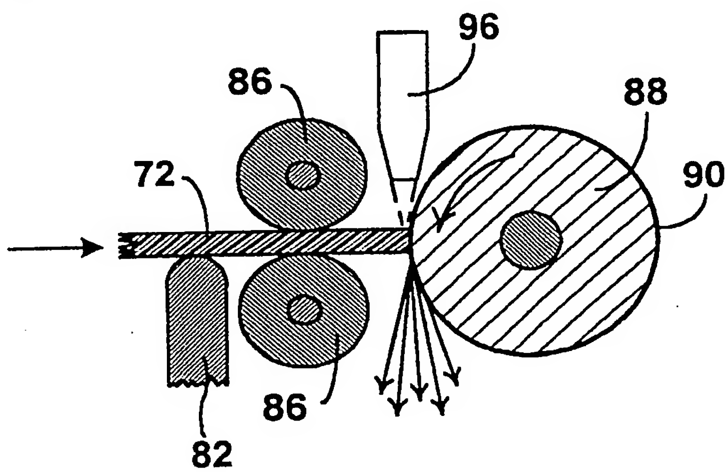


Fig. 4

Fig. 5

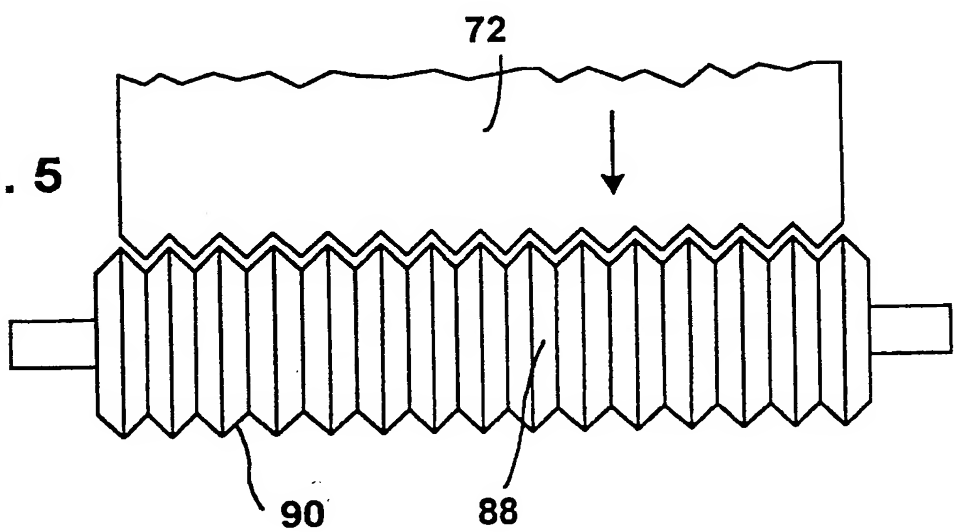


Fig. 1B

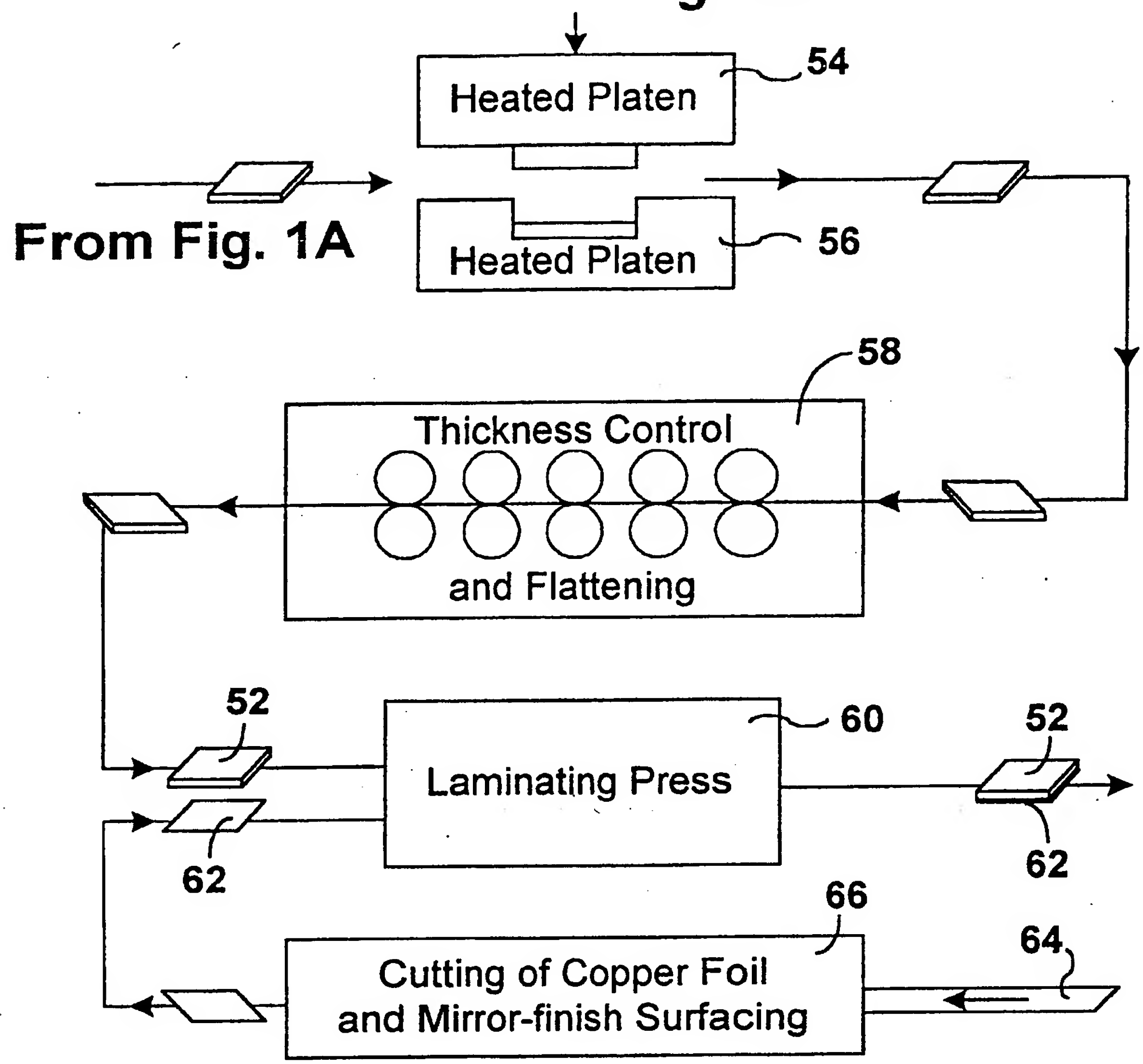
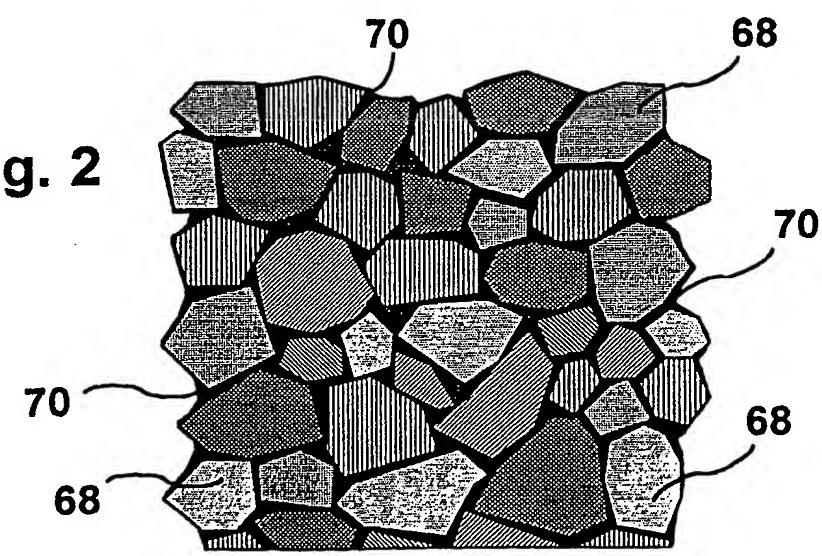

54
Heated Platen
From Fig. 1A
Heated Platen
56
58
Thickness Control
and Flattening
52
Laminating Press
60
52
62
62
66
64
Cutting of Copper Foil
and Mirror-finish Surfacing

Fig. 2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CORRECTED VERSION*

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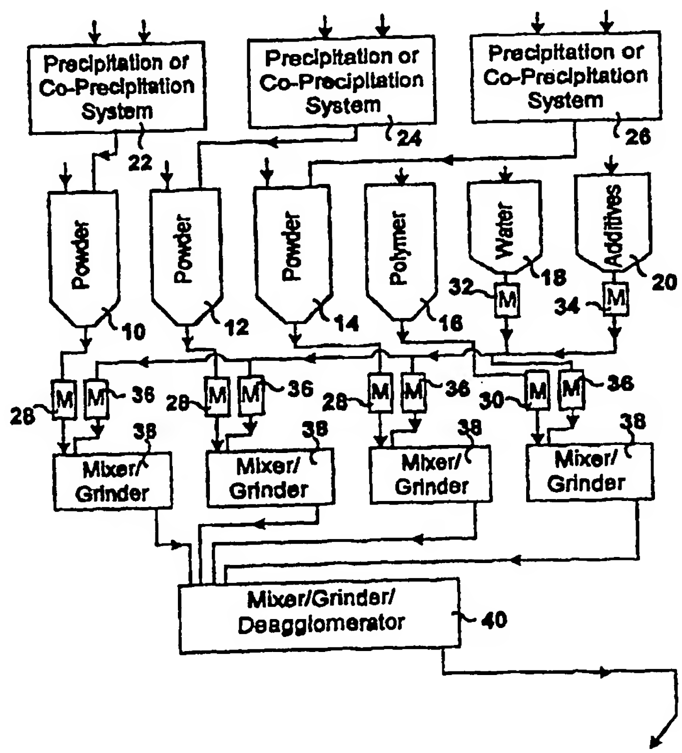
(54) Title: MANUFACTURE OF COMPOSITES OF INORGANIC POWDER AND POLYMER MATERIALS

(57) Abstract

Composite materials comprising at least 70 volume % of particles of finely powdered inorganic material in a matrix of polymer material are made by forming separate mixtures of the components in respective liquid dispersion media, mixing the mixtures to produce thorough dispersion of the components together, dewatering the mixture and forming green articles therefrom. The green articles are heated and pressed to a temperature sufficient to melt the polymer and to a pressure sufficient to disperse the melted polymer into the interstices between the inorganic particles. Mixtures of different inorganic materials may be used to tailor the electrical and physical properties of the final materials. The inorganic materials may be obtained in finely divided form by precipitation or coprecipitation. The articles preferably comprise substrates for use in electronic circuits. The invention also comprises apparatus for carrying out the method and the composite materials that result. Polymer particles of required small size are made by cooling a strip or rod to a brittle fracture temperature and feeding it against a moving grinding surface of coarseness to produce the particles.



*(Referred to in PCT Gazette No. 38/1998, Section II)

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AL	Albania
AM	Armenia
AT	Austria
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AZ	Azerbaijan
BA	Bosnia and Herzegovina
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DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
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NO	Norway
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TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

CORRECTED VERSION*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B23P 17/00

A3

(11) International Publication Number: WO 98/21272

(43) International Publication Date: 22 May 1998 (22.05.98)

(21) International Application Number: PCT/US97/19104

(22) International Filing Date: 24 October 1997 (24.10.97)

(30) Priority Data:
08/738,612 29 October 1996 (29.10.96) US

(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application
US 08/738,612 (CIP)
Filed on 29 October 1996 (29.10.96)

(71)(72) Applicant and Inventor: HOLL, Richard, A. [CA/US]; 2183 Eastridge Trail, Oxnard, CA 93030 (US).

(81) Designated States: CN, JP, KR, RU, SG, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(88) Date of publication of the international search report: 15 October 1998 (15.10.98)

(54) Title: MANUFACTURE OF COMPOSITES OF INORGANIC POWDER AND POLYMER MATERIALS

(57) Abstract

Composite materials comprising at least 70 volume % of particles of finely powdered inorganic material in a matrix of polymer material are made by forming separate mixtures of the components in respective liquid dispersion media, mixing the mixtures to produce thorough dispersion of the components together, dewatering the mixture and forming green articles therefrom. The green articles are heated and pressed to a temperature sufficient to melt the polymer and to a pressure sufficient to disperse the melted polymer into the interstices between the inorganic particles. Mixtures of different inorganic materials may be used to tailor the electrical and physical properties of the final materials. The inorganic materials may be obtained in finely divided form by precipitation or coprecipitation. The articles preferably comprise substrates for use in electronic circuits.

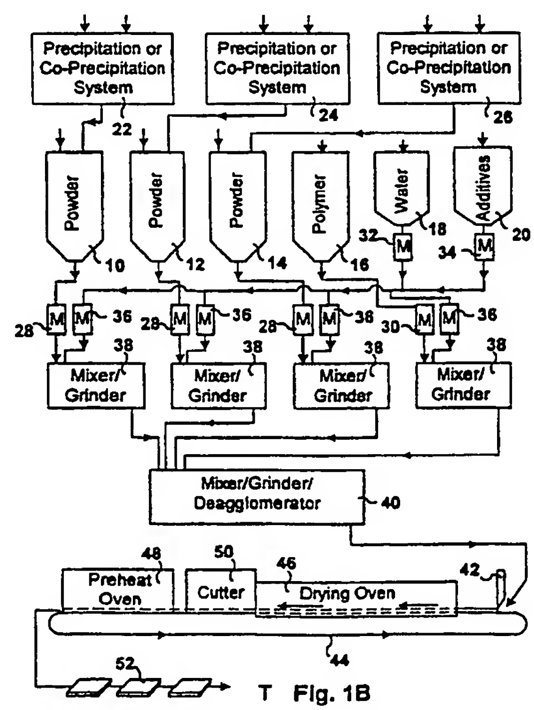

Fig. 1B

*(Referred to in PCT Gazette No. 38/1998, Section II)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19104

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B23P 17/00
US CL :29/527.1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 29/527.1 336/4, 14, 76.6, 76.9, 76.91 428/323, 325, 331, 379, 570, 614

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

MAYA SEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 4,335,180 A (TRAUT) 15 JUNE 1982 (SEE ENTIRE DOCUMENT)	1 AND 2 ----- 3 AND 13-15
A	US 4,954,481 A (DE REGGI ET AL) 04 SEPTEMBER 1990 (SEE ENTIRE DOCUMENT)	1-3,13-15
Y	US 5,011,872 A (LATHAM ET AL) 30 APRIL 1991 (SEE ENTIRE DOCUMENT)	1-3,13-15
A	US 5,024,871 A (ARTHUR ET AL) 18 JUNE 1991 (SEE ENTIRE DOCUMENT)	1-3,13-15

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 12 MARCH 1998	Date of mailing of the international search report 06 MAY 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Sheila Veney For CARL J. ARBES Sheila Veney Paralegal Specialist Telephone No. (703) 308-1857 Group ~~3200~~ 3700

Form PCT/ISA/210 (second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19104

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,182,173 A (SWEI) 26 JANUARY 1993 (SEE ENTIRE DOCUMENT)	1-3,13-15
A	US 5,312,576 A (SWEI ET AL) 17 MAY 1994 (SEE ENTIRE DOCUMENT)	1-3,13-15
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Y	US 5,374,453 A (SWEI ET AL) 20 DECEMBER 1994 (SEE ENTIRE DOCUMENT)	1-3
Y	US 5,506,049 A (SWEI ET AL) 09 APRIL 1996 (SEE ENTIRE DOUCMENT)	1-3
X ----- Y	US 4,849,284 A (ARTHUR ET AL) 18 JULY 1989 (SEE ENTIRE DOCUMENT)	1 AND 2 ------------- 3 AND 14-15
A	US 5,418,056 A (NOGUCHI ET AL) 23 MAY 1995 (SEE ENTIRE DOCUMENT)	1-3 AND 14-15
A	US 5,223,568 A (LANDI ET AL) 29 JUNE 1993 (SEE ENTIRE DOCUMENT)	1-3 AND 14-15
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Y	US 5,393,604 A (SANCHEZ) 28 FEBRUARY 1995 (SEE ENTIRE DOCUMENT)	1-3,14,15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19104

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3 AND14-16

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

Group I claims 1-3 and 14-16.

Group II claims 17-29.

Group III claims 22-24 and 27-29.

Group II is composite material without necessity of the step or means of adding or removing dispersion medium from flowable composite mixture.

Group III recites feeding a cooled strip or rod into contact with moving grinding whereas Groups I and II do not make the composite this way and to use a cooled strip or rod.

Note that those claims found to be unsearchable are improper multiple dependent claims under PCT Rule 6.4 in that they depend from claims tha are themselves multiple dependent claims.

CORRECTED VERSION*

REVISED VERSION**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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Published
With a revised version of the international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report: 15 October 1998 (15.10.98)

(88) Date of publication of the revised version of the international search report: 19 November 1998 (19.11.98)

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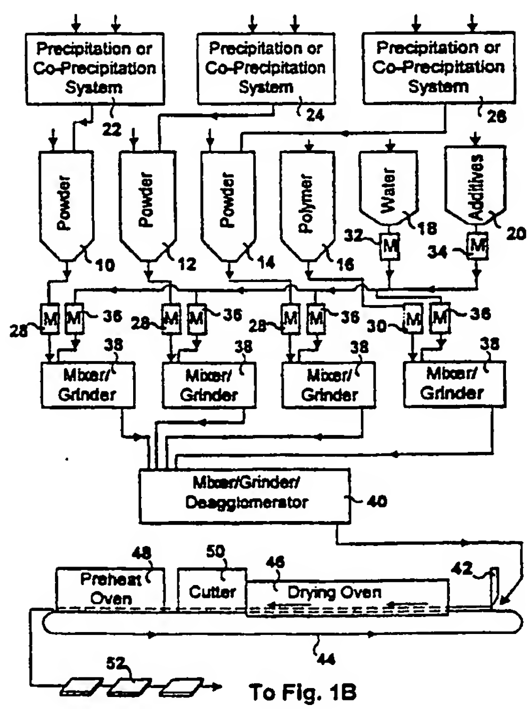

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CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
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GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
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MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
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MN	Mongolia
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UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19104

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :IPC (6) B23P 17/00
US CL :29/527.1
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 29/527.1 336/4, 14, 76.6, 76.9, 76.91 428/323, 325, 331, 379, 570, 614

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

MAYA SEARCH

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 MARCH 1998	29 SEP 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CARL J. ARBES Sheila Veney Paralegal Specialist Technology Center 3700 Telephone No. (703) 308-1857

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19104

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A	US 5,223,568A (LANDI ET AL) 29 JUNE 1993 (SEE ENTIRE DOCUMENT)	1-3 AND 14-15
X	US 5,358,775A (HORN, III) 5 OCTOBER 1994 (SEE ENTIRE DOCUMENT)	1-3
Y	5,393,60 4 A (SANCHEZ) 28 FEBRUARY 1995 (SEE ENTIRE DOCUMENT)	1-3,14,15
X --- Y	JP 01-069,544 A (KOMATSU LTD) 15 MARCH 1989 (SEE ENTIRE DOCUMENT)	17,20 ----------- 18,19,21
Y	SU 1514854 A (LEMINGROD LENSOVET TECH) 15 JANUARY 1989 (SEE ENTIRE DOCUMENT)	22-24, 26-29

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 20, 21, 25, 26, 30 and 31
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I claims 1-3 and 14-16.

Group II claims 17-29.

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1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

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4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.